

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 June 2002 (13.06.2002)

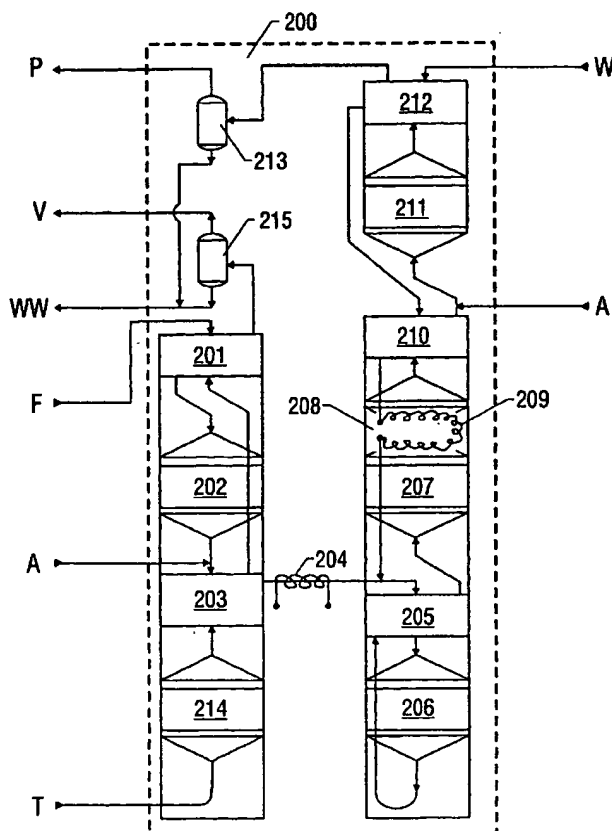
PCT

(10) International Publication Number
WO 02/45839 A1

- (51) International Patent Classification⁷: **B01J 8/04** (74) Agent: **WHITE, Carter, J.**; Howrey Simon Arnold & White, LLP, 750 Bering Drive, Houston, TX 77057-2198 (US).
- (21) International Application Number: **PCT/US01/47374**
- (22) International Filing Date: 5 December 2001 (05.12.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/251,226 5 December 2000 (05.12.2000) US
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent

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(54) Title: **FUEL PROCESSOR FOR PRODUCING A HYDROGEN RICH GAS**



(57) Abstract: An apparatus (200) for carrying out a process of converting hydrocarbon fuel (F) to a hydrogen rich gas (P) including a first heat exchanger (201) for heating the hydrocarbon fuel to produce a heated hydrocarbon fuel, a first desulfurization reactor (202) for reacting the heated hydrocarbon fuel to produce a substantially desulfurized hydrocarbon fuel, a manifold for mixing the substantially desulfurized hydrocarbon fuel with an oxygen containing gas (A) to produce a fuel mixture, a second heat exchanger (203) for heating the fuel mixture to produce a heated fuel mixture, an autothermal reactor (206) including a catalyst for reacting the heated fuel mixture to produce a first hydrogen containing gaseous mixture, a second desulfurization reactor (207) for reacting the first hydrogen containing gaseous mixture to produce a second hydrogen containing gaseous mixture that is substantially desulfurized, a water gas shift reactor (208) for reacting the second hydrogen containing gaseous mixture to produce a third hydrogen containing gaseous mixture with a substantially decreased carbon monoxide content, and selective oxidation reactor (211) for reacting the third hydrogen containing gaseous mixture to produce the hydrogen rich gas (P).

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(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

BACKGROUND OF THE INVENTION

FUEL PROCESSOR FOR PRODUCING A HYDROGEN RICH GAS

Fuel cells provide electricity from chemical oxidation-reduction reactions and possess significant advantages over other forms of power generation in terms of cleanliness and efficiency. Typically, fuel cells employ hydrogen as the fuel and oxygen as the oxidizing agent. The power generation is proportional to the consumption rate of the reactants.

A significant disadvantage which inhibits the wider use of fuel cells is the lack of a widespread hydrogen infrastructure. Hydrogen has a relatively low volumetric energy density and is more difficult to store and transport than the hydrocarbon fuels currently used in most power generation systems. One way to overcome this difficulty is the use of reformers to convert the hydrocarbons to a hydrogen rich gas stream which can be used as a feed for fuel cells.

Hydrocarbon-based fuels, such as natural gas, LPG, gasoline, and diesel, require conversion processes to be used as fuel sources for most fuel cells. Current art uses multi-step processes combining an initial conversion process with several clean-up processes. The initial process is most often steam reforming (SR), autothermal reforming (ATR), catalytic partial oxidation (CPOX), or non-catalytic partial oxidation (POX). The clean-up processes are usually comprised of a combination of desulfurization, high temperature water-gas shift, low temperature water-gas shift, selective CO oxidation, or selective CO methanation. Alternative processes include hydrogen selective membrane reactors and filters.

Despite the above work, there remains a need for a simple unit for converting a hydrocarbon fuel to a hydrogen rich gas stream for use in conjunction with a fuel cell.

SUMMARY OF THE INVENTION

The present invention is generally directed to an apparatus and method for converting hydrocarbon fuel into a hydrogen rich gas. In one illustrative embodiment, the fuel processor of the present invention includes a heat exchanger for heating the hydrocarbon fuel feed prior to entering a desulfurization reactor. The substantially desulfurized hydrocarbon fuel is then mixed in a manifold with an oxygen containing gas to produce a fuel mixture. This fuel mixture is then heated in another heat exchanger

1 before being fed to an autothermal reforming reactor. The resulting hydrogen containing
2 gaseous mixture is then fed to a second desulfurization reactor before being fed to a water
3 gas shift reactor which substantially decreases the carbon monoxide content of the
4 hydrogen containing gaseous mixture. Finally, a selective oxidation reactor can be
5 utilized to produce the hydrogen rich gas.

6 In another illustrative embodiment, the method of the present invention can be
7 utilized for converting hydrocarbon fuel into a hydrogen rich gas by first heating the
8 hydrocarbon fuel to produce a heated hydrocarbon fuel before reacting the heated
9 hydrocarbon fuel in the presence of a catalyst under desulfurization conditions to produce
10 a substantially desulfurized hydrocarbon fuel. The fuel can then be mixed with an
11 oxygen containing gas to produce a fuel mixture. The fuel mixture is then heated before
12 reacting in the presence of a catalyst under autothermal reforming conditions to produce a
13 hydrogen containing gaseous mixture. This mixture is then reacted in the presence of a
14 catalyst under desulfurization conditions to produce a substantially desulfurized hydrogen
15 containing gaseous mixture, which can be further reacted under water gas shift reaction
16 conditions to produce a hydrogen containing gaseous mixture with a carbon monoxide
17 content less than 50 ppm. Finally, this hydrogen stream can be reacted in the presence of
18 a catalyst under selective oxidation reaction conditions of to produce the hydrogen rich
19 gas product.

20

21 BRIEF DESCRIPTION OF THE DRAWINGS

22 The description is presented with reference to the accompanying drawings in
23 which:

24 FIG. 1 depicts a simple process flow diagram for one illustrative embodiment of
25 the present invention.

26 FIG. 2 illustrates one embodiment of a fuel processor of the present invention.

27

28 DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

29 The present invention is generally directed to an apparatus for converting
30 hydrocarbon fuel into a hydrogen rich gas. In a preferred aspect, the apparatus and
31 method described herein relate to a compact processor for producing a hydrogen rich gas

1 stream from a hydrocarbon fuel for use in fuel cells. However, other possible uses are
2 contemplated for the apparatus and method described herein, including any use wherein a
3 hydrogen rich stream is desired. Accordingly, while the invention is described herein as
4 being used in conjunction with a fuel cell, the scope of the invention is not limited to such
5 use.

6 Each of the illustrative embodiments of the present invention describe a fuel
7 processor or a process for using such a fuel processor with the hydrocarbon fuel feed
8 being directed through the fuel processor. The hydrocarbon fuel may be liquid or gas at
9 ambient conditions. As used herein the term "hydrocarbon" includes organic compounds
10 having C-H bonds which are capable of producing hydrogen from a partial oxidation or
11 steam reforming reaction. The presence of atoms other than carbon and hydrogen in the
12 molecular structure of the compound is not excluded. Thus, suitable fuels for use in the
13 method and apparatus disclosed herein include, but are not limited to hydrocarbon fuels
14 such as natural gas, methane, ethane, propane, butane, naphtha, gasoline, and diesel fuel,
15 and alcohols such as methanol, ethanol, propanol, and the like.

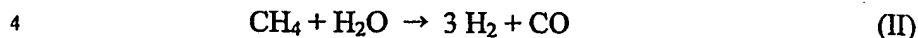
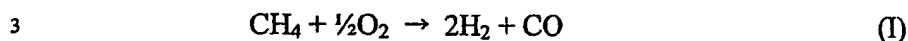
16 The fuel processor feeds include hydrocarbon fuel, oxygen, and water. The
17 oxygen can be in the form of air, enriched air, or substantially pure oxygen. The water
18 can be introduced as a liquid or vapor. The composition percentages of the feed
19 components are determined by the desired operating conditions, as discussed below.

20 The fuel processor effluent stream from of the present invention includes
21 hydrogen and carbon dioxide and can also include some water, unconverted
22 hydrocarbons, carbon monoxide, impurities (e.g. hydrogen sulfide and ammonia) and
23 inert components (e.g., nitrogen and argon, especially if air was a component of the feed
24 stream).

25 Figure 1 depicts a general process flow diagram illustrating the process steps
26 included in the illustrative embodiments of the present invention. One of skill in the art
27 should appreciate that a certain amount of progressive order is needed in the flow of the
28 reactants through the reactors disclosed herein.

29 Process step A is an autothermal reforming process in which two reactions, partial
30 oxidation (formula I, below) and optionally also steam reforming (formula II, below), are
31 combined to convert the feed stream F into a synthesis gas containing hydrogen and

1 carbon monoxide. Formulas I and II are exemplary reaction formulas wherein methane is
2 considered as the hydrocarbon:



5 The partial oxidation reaction occurs very quickly to the complete conversion of
6 oxygen added and produces heat. The steam reforming reaction occurs slower and
7 consumes heat. A higher concentration of oxygen in the feed stream favors partial
8 oxidation whereas a higher concentration of water vapor favors steam reforming.
9 Therefore, the ratios of oxygen to hydrocarbon and water to hydrocarbon become
10 characterizing parameters. These ratios affect the operating temperature and hydrogen
11 yield.

12 The operating temperature of the autothermal reforming step can range from
13 about 550°C to about 900°C, depending on the feed conditions and the catalyst. The
14 invention uses a catalyst bed of a partial oxidation catalyst with or without a steam
15 reforming catalyst. The catalyst may be in any form including pellets, spheres, extrudate,
16 monoliths, and the like. Partial oxidation catalysts should be well known to those with
17 skill in the art and are often comprised of noble metals such as platinum, palladium,
18 rhodium, and/or ruthenium on an alumina washcoat on a monolith, extrudate, pellet or
19 other support. Non-noble metals such as nickel or cobalt have been used. Other
20 washcoats such as titania, zirconia, silica, and magnesia have been cited in the literature.
21 Many additional materials such as lanthanum, cerium, and potassium have been cited in
22 the literature as "promoters" that improve the performance of the partial oxidation
23 catalyst.

24 Steam reforming catalysts should be known to those with skill in the art and can
25 include nickel with amounts of cobalt or a noble metal such as platinum, palladium,
26 rhodium, ruthenium, and/or iridium. The catalyst can be supported, for example, on
27 magnesia, alumina, silica, zirconia, or magnesium aluminate, singly or in combination.
28 Alternatively, the steam reforming catalyst can include nickel, preferably supported on
29 magnesia, alumina, silica, zirconia, or magnesium aluminate, singly or in combination,
30 promoted by an alkali metal such as potassium.

1 Process step B is a cooling step for cooling the synthesis gas stream from process
2 step A to a temperature of from about 200°C to about 600°C, preferably from about
3 300°C to about 500°C, and more preferably from about 375°C to about 425°C, to
4 optimize the temperature of the synthesis gas effluent for the next step. This cooling may
5 be achieved with heat sinks, heat pipes or heat exchangers depending upon the design
6 specifications and the need to recover / recycle the heat content of the gas stream. One
7 illustrative embodiment for step B is the use of a heat exchanger utilizing feed stream F
8 as the coolant circulated through the heat exchanger. The heat exchanger can be of any
9 suitable construction known to those with skill in the art including shell and tube, plate,
10 spiral, etc. Alternatively, or in addition thereto, cooling step B may be accomplished by
11 injecting additional feed components such as fuel, air or water. Water is preferred
12 because of its ability to absorb a large amount of heat as it is vaporized to steam. The
13 amounts of added components depend upon the degree of cooling desired and are readily
14 determined by those with skill in the art.

15 Process step C is a purifying step. One of the main impurities of the hydrocarbon
16 stream is sulfur, which is converted by the autothermal reforming step A to hydrogen
17 sulfide. The processing core used in process step C preferably includes zinc oxide and/or
18 other material capable of absorbing and converting hydrogen sulfide, and may include a
19 support (e.g., monolith, extrudate, pellet etc.). Desulfurization is accomplished by
20 converting the hydrogen sulfide to water in accordance with the following reaction
21 formula III:

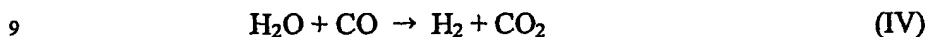


23 Other impurities such as chlorides can also be removed. The reaction is
24 preferably carried out at a temperature of from about 300°C to about 500°C, and more
25 preferably from about 375°C to about 425°C. Zinc oxide is an effective hydrogen sulfide
26 absorbent over a wide range of temperatures from about 25°C to about 700°C and affords
27 great flexibility for optimizing the sequence of processing steps by appropriate selection
28 of operating temperature.

29 The effluent stream may then be sent to a mixing step D in which water is
30 optionally added to the gas stream. The addition of water lowers the temperature of the
31 reactant stream as it vaporizes and supplies more water for the water gas shift reaction of

1 process step E (discussed below). The water vapor and other effluent stream components
2 are mixed by being passed through a processing core of inert materials such as ceramic
3 beads or other similar materials that effectively mix and/or assist in the vaporization of
4 the water. Alternatively, any additional water can be introduced with feed, and the
5 mixing step can be repositioned to provide better mixing of the oxidant gas in the CO
6 oxidation step G disclosed below.

7 Process step E is a water gas shift reaction that converts carbon monoxide to
8 carbon dioxide in accordance with formula IV:



10 This is an important step because carbon monoxide, in addition to being highly
11 toxic to humans, is a poison to fuel cells. The concentration of carbon monoxide should
12 preferably be lowered to a level that can be tolerated by fuel cells, typically below 50
13 ppm. Generally, the water gas shift reaction can take place at temperatures of from
14 150°C to 600°C depending on the catalyst used. Under such conditions, most of the
15 carbon monoxide in the gas stream is converted in this step.

16 Low temperature shift catalysts operate at a range of from about 150°C to about
17 300°C and include for example, copper oxide, or copper supported on other transition
18 metal oxides such as zirconia, zinc supported on transition metal oxides or refractory
19 supports such as silica, alumina, zirconia, etc., or a noble metal such as platinum,
20 rhenium, palladium, rhodium or gold on a suitable support such as silica, alumina,
21 zirconia, and the like.

22 High temperature shift catalysts are preferably operated at temperatures ranging
23 from about 300° to about 600°C and can include transition metal oxides such as ferric
24 oxide or chromic oxide, and optionally including a promoter such as copper or iron
25 silicide. Also included, as high temperature shift catalysts are supported noble metals
26 such as supported platinum, palladium and/or other platinum group members.

27 The processing core utilized to carry out this step can include a packed bed of
28 high temperature or low temperature shift catalyst such as described above, or a
29 combination of both high temperature and low temperature shift catalysts. The process
30 should be operated at any temperature suitable for the water gas shift reaction, preferably
31 at a temperature of from 150°C to about 400°C depending on the type of catalyst used.

1 Optionally, a cooling element such as a cooling coil may be disposed in the processing
2 core of the shift reactor to lower the reaction temperature within the packed bed of
3 catalyst. Lower temperatures favor the conversion of carbon monoxide to carbon
4 dioxide. Also, a purification processing step C can be performed between high and low
5 shift conversions by providing separate steps for high temperature and low temperature
6 shift with a desulfurization module between the high and low temperature shift steps.

7 Process step F is a cooling step performed in one embodiment by a heat
8 exchanger. The heat exchanger can be of any suitable construction including shell and
9 tube, plate, spiral, etc. Alternatively a heat pipe or other form of heat sink may be
10 utilized. The goal of the heat exchanger is to reduce the temperature of the gas stream to
11 produce an effluent having a temperature preferably in the range of from about 90°C to
12 about 150°C.

13 Oxygen is added to the process in step F. The oxygen is consumed by the
14 reactions of process step G described below. The oxygen can be in the form of air,
15 enriched air, or substantially pure oxygen. The heat exchanger may by design provide
16 mixing of the air with the hydrogen rich gas. Alternatively, the embodiment of process
17 step D may be used to perform the mixing.

18 Process step G is an oxidation step wherein almost all of the remaining carbon
19 monoxide in the effluent stream is converted to carbon dioxide. The processing is carried
20 out in the presence of a catalyst for the oxidation of carbon monoxide and may be in any
21 suitable form, such as pellets, spheres, monolith, etc. Oxidation catalysts for carbon
22 monoxide are known and typically include noble metals (e.g., platinum, palladium)
23 and/or transition metals (e.g., iron, chromium, manganese), and/or compounds of noble
24 or transition metals, particularly oxides. A preferred oxidation catalyst is platinum on an
25 alumina washcoat. The washcoat may be applied to a monolith, extrudate, pellet or other
26 support. Additional materials such as cerium or lanthanum may be added to improve
27 performance. Many other formulations have been cited in the literature with some
28 practitioners claiming superior performance from rhodium or alumina catalysts.
29 Ruthenium, palladium, gold, and other materials have been cited in the literature as being
30 active for this use.

1 Two reactions occur in process step G: the desired oxidation of carbon monoxide
2 (formula V) and the undesired oxidation of hydrogen (formula VI) as follows:



5 The preferential oxidation of carbon monoxide is favored by low temperatures. Since
6 both reactions produce heat it may be advantageous to optionally include a cooling
7 element such as a cooling coil disposed within the process. The operating temperature of
8 process is preferably kept in the range of from about 90°C to about 150°C. Process step
9 G preferably reduces the carbon monoxide level to less than 50 ppm, which is a suitable
10 level for use in fuel cells, but one of skill in the art should appreciate that the present
11 invention can be adapted to produce a hydrogen rich product with of higher and lower
12 levels of carbon monoxide.

13 The effluent exiting the fuel processor is a hydrogen rich gas containing carbon
14 dioxide and other constituents which may be present such as water, inert components
15 (e.g., nitrogen, argon), residual hydrocarbon, etc. Product gas may be used as the feed for
16 a fuel cell or for other applications where a hydrogen rich feed stream is desired.
17 Optionally, product gas may be sent on to further processing, for example, to remove the
18 carbon dioxide, water or other components.

19 One illustrative embodiment of the present invention is depicted. Fuel processor
20 100 of the present invention contains a series of process units for carrying out the general
21 process as described in Figure 1. It is intended that the process units may be used in
22 numerous configurations as is readily apparent to one skilled in the art. Furthermore, the
23 fuel processor described herein is adaptable for use in conjunction with a fuel cell such
24 that the hydrogen rich product gas of the fuel processor described herein is supplied
25 directly to a fuel cell as a feed stream.

26 The process equipment described herein may be fabricated from any material
27 capable of withstanding the operating conditions and chemical environment of the
28 reactions described herein and can include, for example, carbon steel, stainless steel,
29 Inconel, Incoloy, Hastelloy, and the like. The operating pressure for the process units are
30 preferably from about 0 to about 100 psig, although higher pressures may be employed.
31 Ultimately, the operating pressure of the fuel processor depends upon the delivery

1 pressure required by the users of the product hydrogen, namely a fuel cell. For fuel cells
2 operating in the 1 to 20 kW range an operating pressure of 0 to about 100 psig is
3 generally sufficient.

4 Fuel processor 200 as shown in Figure 2 similar to the process diagrammatically
5 illustrated in Figure 1 and described supra. Hydrocarbon fuel feed stream F is introduced
6 to the fuel processor and hydrogen rich product gas P is drawn off. Fuel processor 200
7 includes several process units that each perform a separate operational function and is
8 generally configured as shown in Figure 2. In this illustrative embodiment, the
9 hydrocarbon fuel F enters the first compartment 101 into spiral exchanger 201, which
10 preheats the feed F against fuel cell tail gas T (enters fuel processor 200 at reactor 214).
11 Because of the multiple exothermic reactions that take place within the fuel processor,
12 one of skill in the art should appreciate that several other heat integration opportunities
13 are also plausible in this service. This preheated feed then enters desulfurization reactor
14 202 through a concentric diffuser for near-perfect flow distribution and low pressure drop
15 at the reactor inlet. Reactor 202 contains a desulfurizing catalyst and operates as
16 described in process step C of Figure 1. Note that this step does not accord with the order
17 of process steps as presented in Figure 1. This is a prime example of the liberty that one
18 of skill in the art may exercise in optimizing the process configuration in order to process
19 various hydrocarbon fuel feeds and/or produce a more pure product. Desulfurized fuel
20 from reactor 202 is then collected through a concentric diffuser and mixed with air A,
21 with the mixture being routed to exchanger 203. In this illustrative embodiment,
22 exchanger 203 is a spiral exchanger that heats this mixed fuel/air stream against fuel cell
23 tail gas T (enters fuel processor 200 at reactor 214).

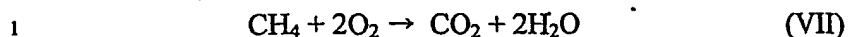
24 The preheated fuel/air mixture then enters the second compartment 102, with the
25 preheat temperature maintained or increased by electric coil heater 204 located between
26 the two compartments. The preheated fuel-air mixture enters spiral exchanger 205, which
27 preheats the stream to autothermal reforming reaction temperature against the
28 autothermal reformer 206 effluent stream. Preheated water (enters fuel processor 200 at
29 exchanger 212) is mixed with the preheated fuel-air stream prior to entering exchanger
30 205. The preheated fuel-air-water mixture leaves exchanger 205 through a concentric
31 diffuser and is then fed to autothermal reformer (ATR) 206, which corresponds to process

1 step A of Figure 1. The diffuser allows even flow distribution at the ATR 206 inlet. The
2 hot hydrogen product from ATR 206 is collected through a concentric diffuser and routed
3 back to exchanger 205 for heat recovery. In this embodiment, exchanger 206 is mounted
4 directly above ATR 206 in order to minimize flow path, thereby reducing energy losses
5 and improving overall energy efficiency. Flow conditioning vanes can be inserted at
6 elbows in order to achieve low pressure drop and uniform flow through ATR 206.

7 The cooled hydrogen product from exchanger 205 is then routed through a
8 concentric diffuser to desulfurization reactor 207, which corresponds to process step C of
9 Figure 1. The desulfurized product is then fed to catalytic shift reactor 208, which
10 corresponds with Process Step E in Figure 1. Cooling coil 209 is provided to control the
11 exothermic shift reaction temperature, which improves CO conversion leading to higher
12 efficiency. In this embodiment, cooling coil 209 also preheats ATR 206 feed, further
13 improving heat recovery and fuel cell efficiency. The shift reaction product is then
14 collected through a concentric diffuser and is cooled in spiral exchanger 210, which also
15 preheats water feed W.

16 Air A is then introduced to the cooled shift reaction product, which is then routed
17 to a concentric diffuser feeding preferred CO oxidation reactor 211. Reactor 211
18 oxidizes trace CO to CO₂, which corresponds to process step G in Figure 1. Flow
19 conditioning vanes may be inserted at elbows to achieve short flow paths and uniform
20 low pressure drop throughout reactor 211. The effluent purified hydrogen stream is then
21 collected in a concentric diffuser and is sent to exchanger 212 which recovers heat energy
22 into the water feed W. The cooled hydrogen stream is then flashed in separator 213 to
23 remove excess water WW. The hydrogen gas stream P from separator 213 is then
24 suitable for hydrogen users, such as a fuel cell.

25 In the embodiment described in Figure 2, the combined anode and cathode vent
26 gas streams from a fuel cell are introduced to fuel processor 200 for heat recovery from
27 the unconverted hydrogen in the fuel cell. Integration of the fuel cell with the fuel
28 processor considerably improves the overall efficiency of electricity generation from the
29 fuel cell. The fuel cell tail gas T flows through a concentric diffuser to anode tail gas
30 oxidizer (ATO) 214. Hydrogen, and possibly a slip stream of methane and other light
31 hydrocarbons are catalytically oxidized according to:



3 Equations VII and VIII take place in ATO 214, which can be a fixed bed reactor
4 composed of catalyst pellets on beads, or preferably a monolithic structured catalyst. The
5 hot reactor effluent is collected through a concentric diffuser and is routed to exchanger
6 203 for heat recovery with the combined fuel/air mixture from reactor 202. Heat from
7 the fuel cell tail gas stream T is then further recovered in exchanger 201 before being
8 being flashed in separator 215. The separated water is connected to the processor
9 effluent water stream WW and the vent gas is then vented to the atmosphere.

10 Such a skilled person in the art should also appreciate that the present invention
11 also encompasses the following illustrative embodiments. One such illustrative
12 embodiment is an apparatus for converting hydrocarbon fuel into a hydrogen rich gas,
13 comprising a manifold for mixing the hydrocarbon fuel with an oxygen-containing gas to
14 give a fuel mixture, an autothermal reactor including a catalyst for reacting the fuel
15 mixture under autothermal reforming conditions to give a hydrogen containing gaseous
16 mixture, a water gas shift reactor including a catalyst for reacting the hydrogen
17 containing gaseous mixture under water gas shift reaction conditions to give an
18 intermediate hydrogen containing gaseous mixture with a substantially reduced carbon
19 monoxide content, and a selective oxidation reactor including a catalyst for reacting the
20 intermediate hydrogen containing gaseous mixture under selective oxidation reaction
21 conditions to produce the hydrogen rich gas. A preferred aspect of this embodiment
22 includes a heat exchanger for heating the hydrocarbon fuel prior to feeding the
23 hydrocarbon fuel feed to the manifold. Another preferred aspect of this embodiment is a
24 desulfurization reactor including a catalyst for reacting the heated hydrocarbon fuel under
25 desulfurization conditions to produce a substantially desulfurized hydrocarbon fuel feed
26 to the manifold. Yet another preferred aspect of this embodiment includes a heat
27 exchanger for heating the fuel mixture prior to feeding the autothermal reactor. Yet
28 another preferred aspect of this embodiment includes another desulfurization reactor
29 including a catalyst for reacting the hydrogen containing gaseous mixture under
30 desulfurization conditions to produce a substantially desulfurized hydrogen containing
31 gaseous mixture feed to the water gas shift reactor. Yet another preferred aspect of this

1 embodiment is an anode tail gas oxidizer including a catalyst for reacting the unconverted
2 hydrogen from a fuel cell under oxidation conditions to create a hot anode tail gas
3 oxidizer effluent. This hot anode tail gas oxidizer effluent can be used to heat integrate
4 with the process and improve the overall energy efficiency of the apparatus.

5 Another illustrative embodiment is an apparatus for converting hydrocarbon fuel
6 into a hydrogen rich gas, comprising a first heat exchanger for heating the hydrocarbon
7 fuel to produce a heated hydrocarbon fuel, a first desulfurization reactor for reacting the
8 heated hydrocarbon fuel to produce a substantially desulfurized hydrocarbon fuel, a
9 manifold for mixing the substantially desulfurized hydrocarbon fuel with an oxygen
10 containing gas to produce a fuel mixture, a second heat exchanger for heating the fuel
11 mixture to produce a heated fuel mixture, an autothermal reactor including a catalyst for
12 reacting the heated fuel mixture to produce a first hydrogen containing gaseous mixture, a
13 second desulfurization reactor for reacting the first hydrogen containing gaseous mixture
14 to produce a second hydrogen containing gaseous mixture that is substantially
15 desulfurized, a water gas shift reactor for reacting the second hydrogen containing
16 gaseous mixture to produce a third hydrogen containing gaseous mixture with a
17 substantially decreased carbon monoxide content, and a selective oxidation reactor for
18 reacting the third hydrogen containing gaseous mixture to produce the hydrogen rich gas.
19 Yet another preferred aspect of this embodiment is an anode tail gas oxidizer including a
20 catalyst for reacting the unconverted hydrogen from a fuel cell under oxidation conditions
21 to create a hot anode tail gas oxidizer effluent. This hot anode tail gas oxidizer effluent
22 can be used to heat integrate with the process and improve the overall energy efficiency
23 of the apparatus.

24 Yet another illustrative embodiment of the present invention is a process for
25 converting hydrocarbon fuel into a hydrogen rich gas by mixing the hydrocarbon fuel
26 with an oxygen containing gas to produce a fuel mixture, then reacting the fuel mixture in
27 the presence of a catalyst under autothermal reforming reaction conditions to produce a
28 hydrogen containing gaseous mixture, then reacting the hydrogen containing gaseous
29 mixture in the presence of a catalyst under water gas shift reaction conditions to produce
30 an intermediate hydrogen containing gaseous mixture with a substantially reduced carbon
31 monoxide content, and then reacting the intermediate hydrogen containing gaseous

1 mixture in the presence of a catalyst under selective oxidation conditions to produce the
2 hydrogen rich gas. A preferred aspect of this embodiment includes heating the
3 hydrocarbon fuel before the mixing step. Another preferred aspect of this embodiment is
4 reacting the heated hydrocarbon fuel in the presence of a catalyst under desulfurization
5 conditions to substantially desulfurize the hydrocarbon fuel prior to the mixing step. Yet
6 another preferred aspect of this embodiment includes heating the fuel mixture prior to the
7 first reaction step. Another preferred aspect of this embodiment includes reacting the
8 hydrogen containing gaseous mixture in the presence of a catalyst under desulfurization
9 reaction conditions to substantially desulfurize the hydrogen containing gaseous mixture
10 prior to the second reaction step. It is intended that this embodiment be able to reduce the
11 carbon monoxide concentration in the hydrogen rich gas to less than 50 ppm. Yet
12 another preferred aspect of this embodiment is utilizing an anode tail gas oxidizer
13 including a catalyst for reacting the unconverted hydrogen from a fuel cell under
14 oxidation conditions to create a hot anode tail gas oxidizer effluent. This hot anode tail
15 gas oxidizer effluent can be used to heat integrate with the process and improve the
16 overall energy efficiency of the apparatus.

17 Yet another illustrative embodiment of the present invention is a method for
18 converting hydrocarbon fuel into a hydrogen rich gas by heating the hydrocarbon fuel to
19 produce a heated hydrocarbon fuel, then reacting the heated hydrocarbon fuel in the
20 presence of a catalyst under desulfurization conditions to produce a substantially
21 desulfurized hydrocarbon, then mixing the substantially desulfurized hydrocarbon with
22 an oxygen containing gas to produce a fuel mixture, then heating the fuel mixture to
23 produce a heated fuel mixture, then reacting the heated fuel mixture in the presence of a
24 catalyst under auto thermal reforming conditions to produce a first hydrogen containing
25 gaseous mixture, then reacting the first hydrogen containing gaseous mixture in the
26 presence of a catalyst under desulfurization conditions to produce a second hydrogen
27 containing gaseous mixture that is substantially desulfurized, then reacting the second
28 hydrogen containing gaseous mixture with a catalyst under water gas shift reaction
29 conditions to produce a third hydrogen containing gaseous mixture with a substantially
30 reduced carbon monoxide content, and then reacting the third hydrogen containing
31 gaseous mixture in the presence of a catalyst under selective oxidation reaction

1 conditions of to produce the hydrogen rich gas. It is intended that this embodiment be
2 able to reduce the carbon monoxide concentration in the hydrogen rich gas to less than
3 50 ppm. Yet another preferred aspect of this embodiment is utilizing an anode tail gas
4 oxidizer including a catalyst for reacting the unconverted hydrogen from a fuel cell under
5 oxidation conditions to create a hot anode tail gas oxidizer effluent. This hot anode tail
6 gas oxidizer effluent can be used to heat integrate with the process and improve the
7 overall energy efficiency of the apparatus.

8 While the apparatus and methods of this invention have been described in terms
9 of preferred embodiments, it will be apparent to those of skill in the art that variations
10 may be applied to the process described herein without departing from the concept and
11 scope of the invention. All such similar substitutes and modifications apparent to those
12 skilled in the art are deemed to be within the scope and concept of the invention.

1 **WHAT IS CLAIMED IS:**

- 2
- 3 1. An apparatus for converting hydrocarbon fuel into a hydrogen rich gas comprising:
- 4 a manifold for mixing the hydrocarbon fuel with an oxygen containing gas to give a
- 5 fuel mixture;
- 6 an autothermal reactor including a catalyst for reacting the fuel mixture under
- 7 autothermal reforming conditions to give a hydrogen containing gaseous mixture;
- 8 a water gas shift reactor including a catalyst for reacting the hydrogen containing
- 9 gaseous mixture under water gas shift reaction conditions to give an intermediate
- 10 hydrogen containing gaseous mixture with a substantially reduced carbon
- 11 monoxide content; and
- 12 a selective oxidation reactor including a catalyst for reacting the intermediate
- 13 hydrogen containing gaseous mixture under selective oxidation reaction
- 14 conditions to produce the hydrogen rich gas.
- 15
- 16 2. The apparatus according to claim 1, further comprising a heat exchanger for heating
- 17 the hydrocarbon fuel into a heated hydrocarbon fuel, wherein the heated hydrocarbon
- 18 fuel becomes the hydrocarbon fuel feed to the manifold.
- 19
- 20 3. The apparatus according to claim 2, further comprising a desulfurization reactor
- 21 including a catalyst for reacting the heated hydrocarbon fuel under desulfurization
- 22 conditions to produce a substantially desulfurized hydrocarbon fuel, wherein the
- 23 substantially desulfurized hydrocarbon fuel becomes the hydrocarbon fuel feed to the
- 24 manifold.
- 25
- 26 4. The apparatus according to claim 1, further comprising a heat exchanger for heating
- 27 the fuel mixture to produce a heated fuel mixture, wherein the heated fuel mixture
- 28 becomes the fuel mixture feed to the autothermal reactor.
- 29
- 30 5. The apparatus according to claim 4, further comprising a desulfurization reactor
- 31 including a catalyst for reacting the hydrogen containing gaseous mixture under

- 1 desulfurization conditions to produce a substantially desulfurized hydrogen
2 containing gaseous mixture, wherein the substantially desulfurized hydrogen
3 containing gaseous mixture becomes the hydrogen containing gaseous mixture feed to
4 the water gas shift reactor.
5
- 6 6. The apparatus according to claim 1, wherein the hydrocarbon fuel is selected from the
7 group consisting of natural gas, methane, ethane, propane, butane, liquefied
8 petroleum gas, naphtha, gasoline, kerosene, diesel, methanol, ethanol, propanol, and
9 combinations thereof.
10
- 11 7. The apparatus according to claim 1, wherein the hydrogen rich gas contains less than
12 50 ppm of carbon monoxide.
13
- 14 8. The apparatus according to claim 1, further comprising an anode tail gas oxidizer
15 including a catalyst for reacting the unconverted hydrogen from a fuel cell under
16 oxidation conditions to create a hot anode tail gas oxidizer effluent.
17
- 18 9. The apparatus according to claim 8, wherein the hot anode tail gas oxidizer effluent is
19 heat integrated with the apparatus.
20
- 21 10. An apparatus for converting hydrocarbon fuel into a hydrogen rich gas comprising:
22 a first heat exchanger for heating the hydrocarbon fuel to produce a heated
23 hydrocarbon fuel;
24 a first desulfurization reactor for reacting the heated hydrocarbon fuel to produce a
25 substantially desulfurized hydrocarbon fuel;
26 a manifold for mixing the substantially desulfurized hydrocarbon fuel with an oxygen
27 containing gas to produce a fuel mixture;
28 a second heat exchanger for heating the fuel mixture to produce a heated fuel mixture;
29 an autothermal reactor including a catalyst for reacting the heated fuel mixture to
30 produce a first hydrogen containing gaseous mixture;

- 1 a second desulfurization reactor for reacting the first hydrogen containing gaseous
2 mixture to produce a second hydrogen containing gaseous mixture that is
3 substantially desulfurized;
4 a water gas shift reactor for reacting the second hydrogen containing gaseous mixture
5 to produce a third hydrogen containing gaseous mixture with a substantially
6 decreased carbon monoxide content; and
7 a selective oxidation reactor for reacting the third hydrogen containing gaseous
8 mixture to produce the hydrogen rich gas; and
9
- 10 11. The apparatus according to claim 10, wherein the hydrocarbon fuel is selected from
11 the group consisting of natural gas, methane, ethane, propane, butane, liquefied
12 petroleum gas, naphtha, gasoline, kerosene, diesel, methanol, ethanol, propanol, and
13 combinations thereof.
14
- 15 12. The apparatus according to claim 10, wherein the hydrogen rich gas contains less than
16 50 ppm of carbon monoxide.
17
- 18 13. The apparatus according to claim 10, further comprising an anode tail gas oxidizer
19 including a catalyst for reacting the unconverted hydrogen from a fuel cell under
20 oxidation conditions to create a hot anode tail gas oxidizer effluent.
21
- 22 14. The apparatus according to claim 13, wherein the hot anode tail gas oxidizer effluent
23 is heat integrated with the apparatus.
24
- 25 15. A method for converting hydrocarbon fuel into a hydrogen rich gas, comprising:
26 mixing the hydrocarbon fuel with an oxygen containing gas to produce a fuel
27 mixture;
28 reacting the fuel mixture in the presence of a catalyst under autothermal reforming
29 reaction conditions to produce a hydrogen containing gaseous mixture;
30 reacting the hydrogen containing gaseous mixture in the presence of a catalyst under
31 water gas shift reaction conditions to produce an intermediate hydrogen

1 containing gaseous mixture with a substantially reduced carbon monoxide
2 content; and
3 reacting the intermediate hydrogen containing gaseous mixture in the presence of a
4 catalyst under selective oxidation conditions to produce the hydrogen rich gas.

5
6 16. The method according to claim 15 further comprising heating the hydrocarbon fuel to
7 produce a heated hydrocarbon fuel, wherein the heated hydrocarbon fuel becomes the
8 hydrocarbon fuel feed to the mixing step.

9
10 17. The method according to claim 16 further comprising reacting the heated
11 hydrocarbon fuel in the presence of a catalyst under desulfurization conditions to
12 produce a substantially desulfurized hydrocarbon fuel, wherein the substantially
13 desulfurized hydrocarbon fuel becomes the hydrocarbon fuel feed to the mixing step
14 in a manifold.

15
16 18. The method according to claim 15, further comprising heating the fuel mixture to
17 produce a heated fuel mixture, wherein the heated fuel mixture becomes the fuel
18 mixture feed to the first reaction step.

19
20 19. The method according to claim 15, further comprising reacting the hydrogen
21 containing gaseous mixture in the presence of a catalyst under desulfurization
22 reaction conditions to produce a substantially desulfurized hydrogen containing
23 gaseous mixture, wherein the substantially desulfurized hydrogen containing gaseous
24 mixture becomes the hydrogen containing gaseous mixture feed to the second
25 reaction step.

26
27 20. The method according to claim 15, wherein the hydrocarbon fuel is selected from the
28 group consisting of natural gas, methane, ethane, propane, butane, liquefied
29 petroleum gas, naphtha, gasoline, kerosene, diesel, methanol, ethanol, propanol, and
30 combinations thereof.

31

- 1 21. The method according to claim 15, wherein the hydrogen rich gas contains less than
2 50 ppm of carbon monoxide.
3
- 4 22. The method according to claim 15, further comprising reacting anode tail gas from a
5 fuel cell in the presence of a catalyst under oxidation conditions to produce a hot
6 anode tail gas oxidizer effluent.
7
- 8 23. The method according to claim 22, wherein the hot anode tail gas oxidizer effluent
9 preheats the hydrocarbon fuel.
10
- 11 24. A method for converting hydrocarbon fuel into a hydrogen rich gas, comprising:
12 heating the hydrocarbon fuel to produce a heated hydrocarbon fuel;
13 reacting the heated hydrocarbon fuel in the presence of a catalyst under
14 desulfurization conditions to produce a substantially desulfurized hydrocarbon;
15 mixing the substantially desulfurized hydrocarbon with an oxygen containing gas to
16 produce a fuel mixture;
17 heating the fuel mixture to produce a heated fuel mixture;
18 reacting the heated fuel mixture in the presence of a catalyst under auto thermal
19 reforming conditions to produce a first hydrogen containing gaseous mixture;
20 reacting the first hydrogen containing gaseous mixture in the presence of a catalyst
21 under desulfurization conditions to produce a second hydrogen containing
22 gaseous mixture that is substantially desulfurized;
23 reacting the second hydrogen containing gaseous mixture with a catalyst under water
24 gas shift reaction conditions to produce a third hydrogen containing gaseous
25 mixture with a substantially reduced carbon monoxide content; and
26 reacting the third hydrogen containing gaseous mixture in the presence of a catalyst
27 under selective oxidation reaction conditions of to produce the hydrogen rich gas.
28
- 29 25. The method according to claim 24, wherein the hydrocarbon fuel is selected from the
30 group consisting of natural gas, methane, ethane, propane, butane, liquefied

1 petroleum gas, naphtha, gasoline, kerosene, diesel, methanol, ethanol, propanol, and
2 combinations thereof.

3

4 26. The method according to claim 24, wherein the hydrogen rich gas contains less than
5 50 ppm of carbon monoxide.

6

7 27. The method according to claim 24, further comprising reacting anode tail gas from a
8 fuel cell in the presence of a catalyst under oxidation conditions to produce a hot
9 anode tail gas oxidizer effluent.

10

11 28. The method according to claim 27, wherein the hot anode tail gas oxidizer effluent
12 preheats the hydrocarbon fuel.

13

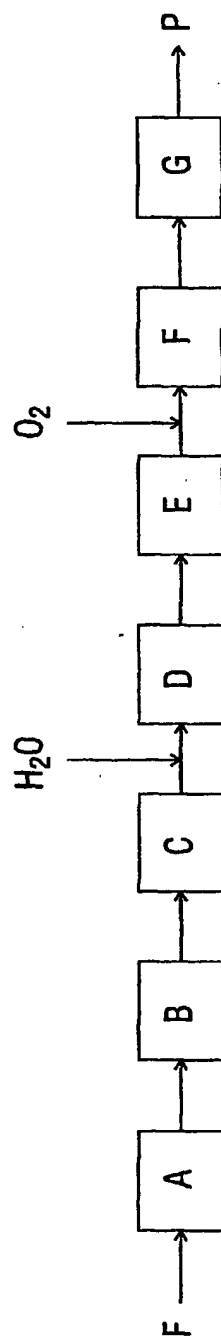


FIG. 1

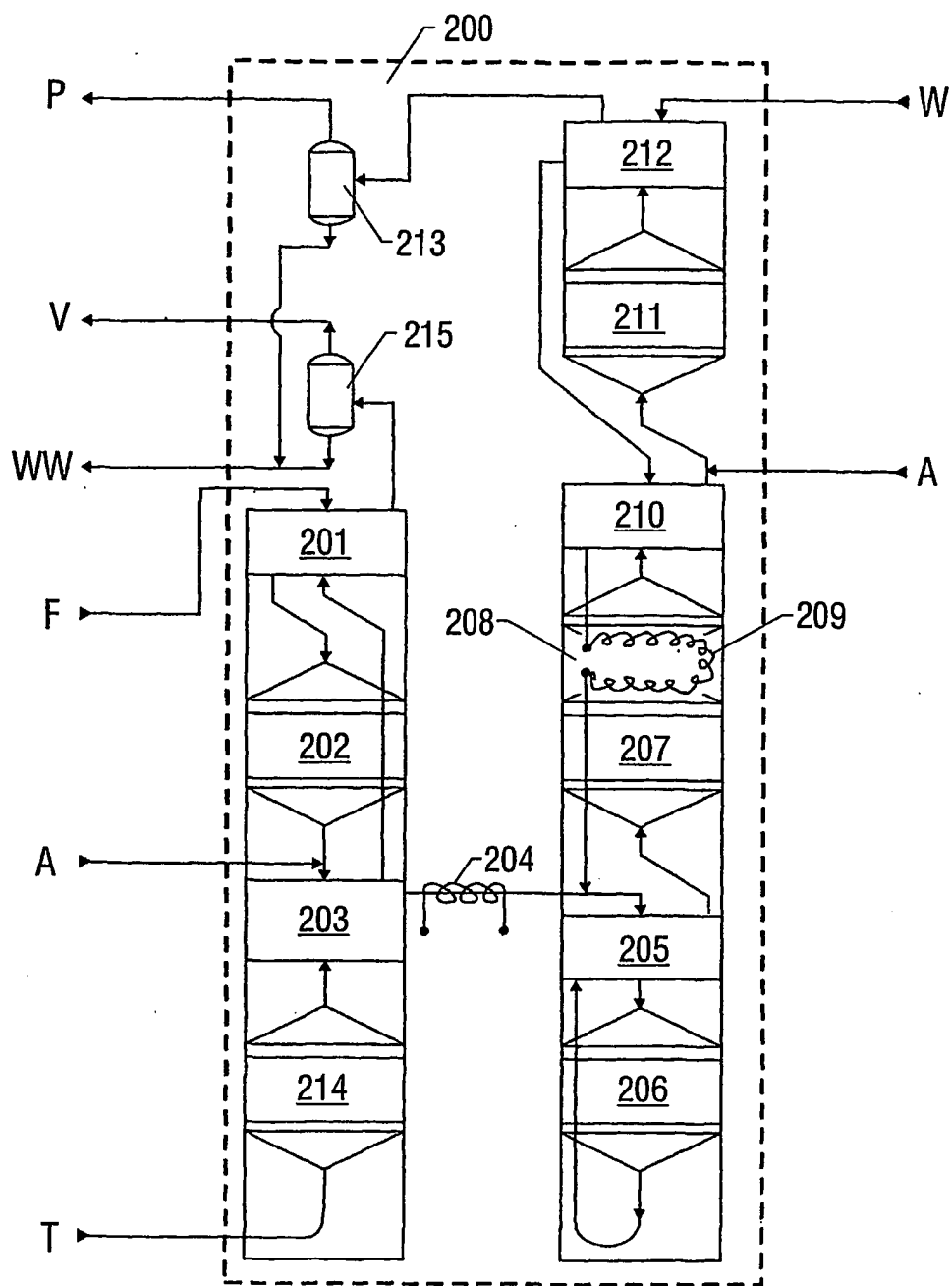


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/47374

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01J 8/04

US CL : 422/188,187,189,190,192,193,194; 48/127.9

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 422/188,187,189,190,192,193,194; 48/127.9

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,363,654 A (FREDERICK et al.) 14 December 1982 (14.12.1982), Fig. 1.	1-28
Y	US 4,522,894 A (HWANG et al.) 11 June 1985 (11.06.1985), Fig. 2 and abstract.	1-28
Y	US 4,976,747 A (SZYDLOWSKI et al.) 11 December 1990 (11.12.1990), Fig. 1.	1-28
Y	US 5,248,566 A (KUMAR et al.) 28 September 1993 (28.09.1993), Fig. 2.	1-28
Y	US 6,086,839 A (AUTENRIETH et al.) 11 July 2000 (11.07.2000), Fig. 1 and abstract.	1-28
A	US 5,132,007 A (MEYER et al.) 21 July 1992 (21.07.1992)	1-28
A	US 5,874,051 A (HEIL et al.) 23 February 1999 (23.02.1999)	1-28
A	US 5,997,594 A (EDLUND et al.) 07 December 1999 (07.12.1999)	1-28
A,P	US 6,238,815 B1 (SKALA et al.) 29 May 2001 (29.05.2001)	1-28



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

06 March 2002 (06.03.2002)

Date of mailing of the international search report

08 APR 2002

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